


Chapter 3

Redox Self–Purification Mechanism of Natural Waters With the Involvement of Thioglycolic Acid and Thiourea


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ABSTRACT

This chapter studied the influence of TGA and TU on the self-purification processes of aquatic systems on model systems, whose composition was modeled to be as close as possible to the natural waters. As a source of irradiation was used the DRT-400 lamp and the Solar Simulator, Oriol model 9119X, the emission spectra of which overlap with the emission spectrum of the Sun. The results of the research show that on irradiation, TGA can regenerate an additional amount of OH radicals, thus contributing to the intensification of water self-purification processes. But in the presence of transition metals, such as Cu (II) and Fe (III), it has been established that the intensity of self-purification processes decreases due to the formation of the mercaptides, whose catalytic activity is low. Unlike TGA, TU leads to decreasing the intensity of the self-purification processes of aquatic systems, through the intense consumption of OH radicals, and at the same time on the interaction with transition metals, such as Cu (II) and Fe (III), form stable complexes with low catalytic activity.

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INTRODUCTION

Decades of research have demonstrated that natural waters represent an unbalanced open kinetic system, with various redox processes involving pollutants, oxidizing agents, metal ions and their complexes, etc. Research in the field has shown that thiol substances, especially those of allochthonous origin, are hardly oxidized by dissolved oxygen, but easily by hydrogen peroxide. Thiol substances reduce or remove the content of hydrogen peroxide, which plays an important role in regulating the redox state of natural waters, thus contributing to the formation of the quasi-reducing state of waters, which is toxic to hydrobionts. At the same time, thiols, upon interaction with transition metal ions, form stable compounds, whose catalytic activity is low. Some thiols, such as thiourea, inhibit the activity of microorganisms in the biological treatment of wastewater. In this context, the main goal of this research was to evaluate the participation of thioglycolic acid (TGA) and thiourea (TU) in redox processes on model systems, to predict their influence on the self-purification capacity of natural aquatic systems.

BACKGROUND

Water is an essential component of the natural environment and the basis of many productive activities, consequently, all human societies have been developed around it. During recent decades, there has been constantly increasing concern about natural water quality and different problems related to the presence, utilization, and management of water resources (Vaseashta et al, 2021). Aquatic systems may be represented as redox catalytic and photochemical open-type multi-component. This fact is largely due to the redox components, the most important of which are: oxygen, hydrogen peroxide, solar radiation, transition metal ions, and complexes, as well as autochthonous and allochthonous reducers (Gladchi et al., 2008; Duca et al., 2008; Bunduchi et al., 2006; Patel et al., 2019).

Dissolved oxygen is the most prevalent oxidative component in natural waters, between 0 and 14 mg/L, and is controlled by two main processes: photosynthesis and biotic and abiotic consumption (Gladchi et al., 2022a; Duca & Travin, 2020; Song et al., 2019; Schmidtko et al., 2017; Liu et al., 2018). Oxygen was the chemical substance that determined the change in the redox state of natural waters from reducing to oxidizing, with the appearance on Earth of autotrophic organisms that produce and eliminate molecular oxygen in the aquatic environment (Foyer et al., 2003). In addition to its vital function, oxygen is also a strong oxidizer, but O₂ is normally inert due to its triplet structure (Duca & Vaseashta, 2020, Vaseashta & Duca, 2022). Therefore, for the involvement of oxygen in oxidation processes, it must be activated, either with sunlight or substances with reducing properties (Larson & Mccord, 1977; Wang et al., 2020). Some of the special components of the chemical composition of natural waters are transition metal ions (Subramanian & Madras, 2017; Lo Conte & Carroll, 2013; Chu et al., 2017; Sun et al., 2011). In the presence of dissolved oxygen, metal ions are in an oxidized state. They help to activate oxygen and hydrogen peroxide, which subsequently engage with different substrates and help to convert them. The following active species are generated in natural waters as a result of the activation of molecular oxygen: ¹O₂, O₂[•], [•]OH, and H₂O₂ (Morris et al., 2022; Mill et al., 1980). The ranges of these species concentrations in natural waters have been determined by the authors of various papers: [¹O₂] = 10⁻¹⁴-10⁻¹² M; [HO₂[•]] = 10⁻⁹-10⁻⁸ M; [[•]OH] = 10⁻¹⁸-10⁻¹⁵ M; [H₂O₂] = 10⁻⁶-10⁻⁵ M (Morris et al., 2022; Patterson & Myers, 1973; Wong et al., 2003; Yuan et al., 2018).

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